Water–based Polyurethane Graphene Oxide Nanocomposites

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Introduction

Graphene – one atom thick, sheets of sp[2]-bonded carbon – has emerged as a new class of nanomaterials (1). Graphene sheets can be manufactured in large quantities by oxidizing graphite, followed by exfoliation of the resulting graphite oxide (GO) (2). The graphene sheets produced by this process are highly oxidized (i.e., graphene oxide sheets), and contain a variety of oxygen groups, such as hydroxyl, epoxide, and carboxylic acids, on the basal planes and at the sheet edges (2). These groups can form strong hydrogen and covalent bonds with a variety of polymer matrices. Further, the large spacing between the graphene oxide sheets facilitate monomer intercalation and polymerization in inter-layer spaces (3). Such capabilities will increase the interfacial strength and potentially provide strong interlocking between the polymer matrix and the graphene sheets.

Combining its exceptional mechanical, thermal and barrier properties with low cost, makes graphene oxide sheet ideal for enhancing multifunctional properties of polymers, as demonstrated in several reviews (2,3). This study investigates the performance of a water-borne polyurethane (PU) coating containing graphene oxide sheets. This class of PU coating is increasingly replacing the solvent-borne counterparts used in many industries. However, the incorporation of graphene oxide sheets to enhance coating properties has not been explored.

Experimental Procedures*

Materials and Water-borne PU Composite Preparation

One-component, water-borne polyurethane was an anionic dispersion of an aliphatic polyester urethane resin in water (50 %, by mass) and in n-methyl-2-pyrrolidone (NMP) (15 %, by mass) (Bayhydrol 110, Bayer MaterialScience LLC). The chemical structure and other ingredients, such as surfactants and additives, in this material are not known. The GO material consisting of graphene oxide sheets was prepared at the University of Texas, Austin, using a process described elsewhere (4). PU nanocomposites containing mass fractions of 0 % (i.e., unfilled), 0.4 %, 0.8 %, 1.2 % and 2 % of GO were prepared following the process illustrated in Figure 1. (Because 60 % of the mass of the as-received GO sample is water, its amounts added to the composites were adjusted accordingly to provide the desired loadings.)
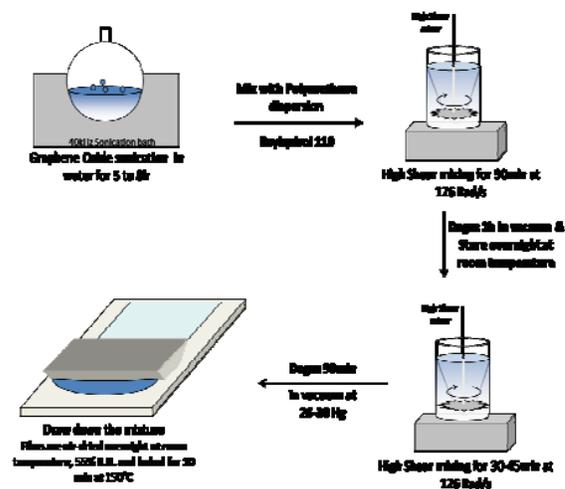

Figure 1. Steps and conditions used to prepare water-borne PU/graphene oxide sheet nanocomposites.

Appropriate amounts of GO (depending on loading) were progressively added to a water-containing flask to provide a concentration of approximately 6 mg GO in 1 ml water. After sonicating (at 40 kHz) for 5 h to 8 h (longer time for higher GO loading) in an ultra-sonic bath, the water-dispersed GO was placed in a beaker containing an appropriate amount of water-borne PU. The PU/GO mixture in water and NMP was mixed in a high shear mixer (Dispermat, VMA) at 126 rad/s (1200 rpm) for 1 h 30 min followed by degassing in vacuum for 1 h and storing at room temperature for 12 h. It is expected that the GO was mostly exfoliated into graphene oxide sheets at this stage. After undergoing further high-shear mixing for 45 min followed by degassing for 1 h 30 min, the viscous water-borne PU/GO mixture was applied onto a polyethylene terephthalate (Mylar) sheet, followed by film spreading using a drawdown blade. The nanocomposite films were cured for 12 h at room temperature, followed by 10 min at 150 °C in an air-circulating oven. The cured films had a thickness between 105 μm and 150 μm.

Characterization of Water-borne PU/GO Nanocomposite Properties.

Microstructure, mechanical properties, thermal stability, oxygen permeability, and water vapor sorption of water-borne PU/GO nanocomposites were characterized. Microstructure was characterized by field-emission scanning electron microscopy (FE-SEM) on cryo-fractured surfaces.

Tensile tests were performed using a dynamic mechanical thermal analyzer (DMTA) in transient mode on dog bone samples having a 20 mm gage length and a 3.30 mm width at a 0.5 mm/s extension rate. The glass transition temperature was measured by DMTA in the temperature ramp mode at 3°C/min heating rate, 1 Hz, and 0.1% strain that was within the linear viscoelastic region. Thermal stability was assessed by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under N_2. Oxygen permeability was measured on 20 mm x 50 mm film samples using a custom-modified Oxtran-100 coulometric permeation apparatus, and the O_2 analysis was relied on reaction between O_2 and H_2 utilizing a catalysis-based sensor (5).

Results and Discussion

Microstructure

Figure 2 displays FE-SEM images for fractured surfaces of water-borne PU nanocomposites containing 0.4 % and 2 % mass fractions of GO. These images provide useful information about exfoliation, dispersion, and adhesion between graphene oxide sheets and the PU matrix. The edges of the graphene sheets are clearly observed, which have a thickness of approximately between 8 and 12 nm, indicating that the sonification/high-shear mixing procedure was satisfactory to exfoliate GO into single or bundles of graphene oxide sheets. For the 2 % mass fraction sample, some air gaps between the sheets are observed (arrow in Figure 2b, high magnification). This evidence suggests that the exfoliation of the higher loading mixture was not complete and, thus, the spaces between some sheets were not filled with urethane molecules during mixing.
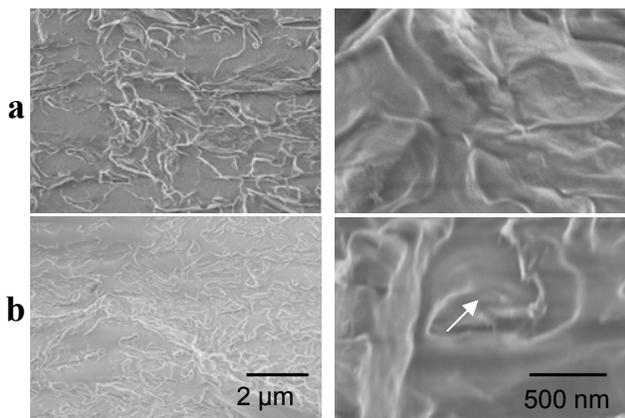

Figure 2. FE-SEM images at two magnifications of fractured surfaces for water-borne PU containing 0.4 % (a) and 2 % (b) mass fractions of GO.

As seen in Fig. 2, although bundles of graphene oxide sheets exist, they were well dispersed in this water-borne PU. In addition, high magnification images, show no evidence of delamination/separation between the polymer and the sheets or dewetting of the PU on the sheet basal planes. This is expected because the NH-C=O groups in the urethane coating can form strong hydrogen bonds with polar functional groups on the graphene oxide sheet surface.

Thermo-mechanical Properties

Figure 3 shows the tanδ as a function of temperature measured by DMTA. This polymer exhibits two glass transition temperatures(T_g), corresponding to the soft segment and hard segment in the PU. The low T_g near -18 °C corresponding to the soft segment was essentially unchanged by the GO incorporation, suggesting that chain mobility in the soft segments was not affected by this nanofiller. However, the high T_g decreases substantially with GO incorporation, from 88 °C for the unfilled PU to 66 °C for the 1.2 % loading, suggesting that graphene oxide sheets reduce molecular ordering in the hard segments, allowing PU polymer chains to move more freely.
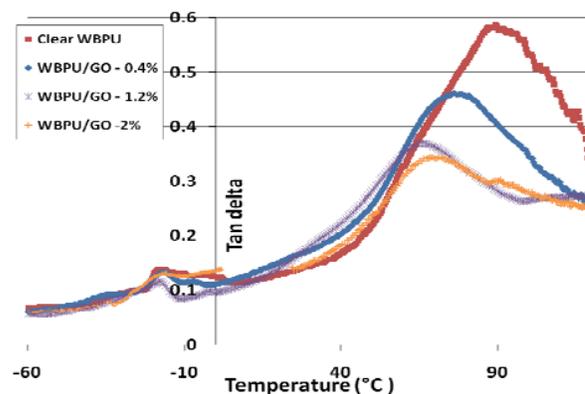

Figure 3. Tanδ vs. temperature curves of water-borne PU containing different amounts of GO.

Figure 4 shows the stress-strain behavior and mechanical properties for water-borne PU nanocomposites containing different amounts of GO (the strain energy density data were taken from the areas underneath the stress-strain curves, and indicates material toughness). Except for the highest loading level, both the strain energy density and elongation to break decrease with increasing GO loading,. However, as seen in the stress-strain curves, the composite (for all loading levels studied) still behaves as a ductile material. On the other hand, except for the low loading levels (<0.8 %), both the yield stress and the modulus increase markedly with an addition of GO. For example, the Young modulus increases by 45 % and 167 % at 1.2 % and 2 % loading, respectively.

The large modulus increase indicates an efficient stress transfer in the water-borne PU/GO nanocomposites. This is likely due to two main factors: 1) a strong molecular interaction between PU and graphene oxide sheets, resulting from the abundance of -polar groups on the sheets, the strong hydrogen bonds formed between these groups and the PU chains, and the increased interfacial area produced by good dispersion, and 2) the ability of urethane molecules to intercalate into the spaces between graphene oxide sheets during mixing, thus increasing the number of interaction sites and providing a strong mechanical interlocking between the polymer and the nanofillers.
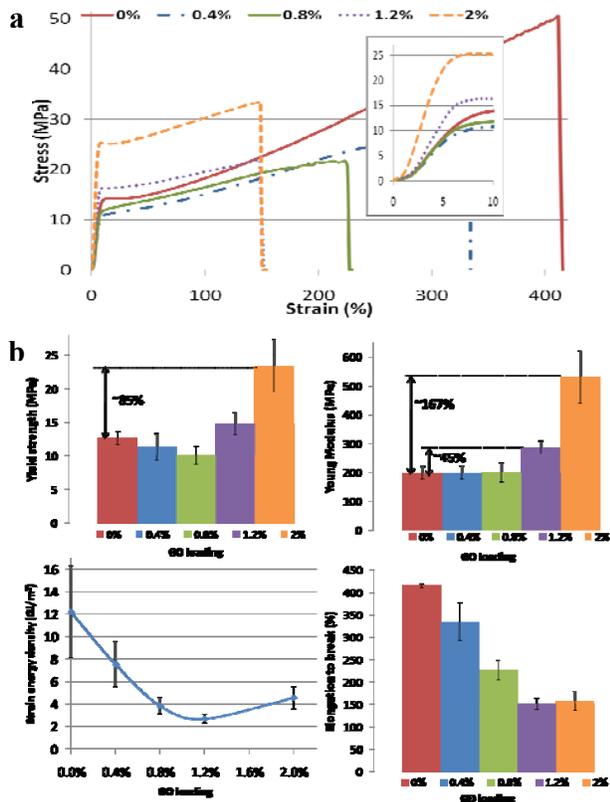
a

b

Figure 4. a) Stress-strain curves, with inset of the expanded small strain region, for water-borne PU containing different GO amounts, and b) mechanical properties as a function of GO loading in water-borne PU. All results in Fig. 4b are the average of 20 specimens, and error bars represent one standard deviation.

Oxygen Permeability

The effect of GO loading on oxygen permeability of water-borne PU is illustrated in Figure 5. The permeability is expressed as the oxygen volume (reduced to normal conditions) that passes through a unit thickness of the film, per unit area, per second (cm^3 (STP)cm^{-1}, s^{-1} $cmHg^{-1}$).
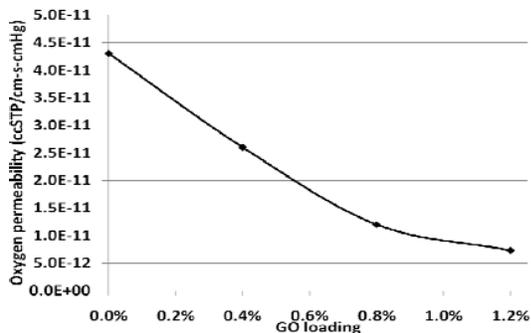

Figure 5. O_2 permeability as a function of GO loading in water-borne PU.

Although this result was obtained from only one sample for each loading level, the measurement is highly re-

producible with coefficient of variation <10 % (5). The permeability of O_2 decreases with increasing GO loading. At 1.2 % loading, the permeability of oxygen is 17 times lower than that of the unfilled PU, indicating that high-aspect ratio graphene oxide sheets can provide an effective barrier to oxygen transport in this polymer.

Thermal stability

Figure 6 shows TGA and its derivative (DTG) curves for water-borne PU containing different GO amounts. The degradation temperature at maximum rate of mass loss (i.e., peak of the DTG curve) increases progressively with increasing GO loading, from 321 °C for unfilled PU to 343 °C for 2 % loading, suggesting that the thermal stability of this PU is enhanced by graphene oxide sheets.
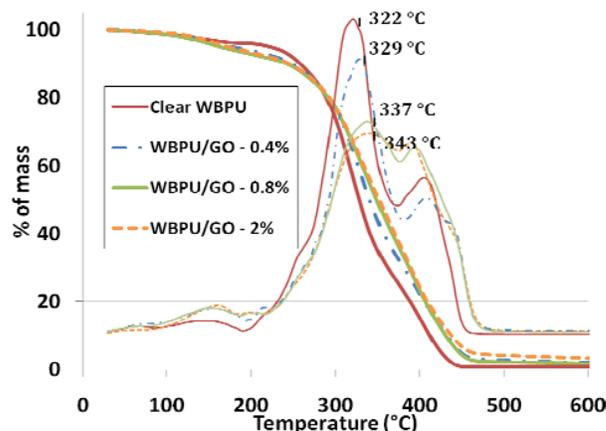

Figure 6. TGA and its derivative curves (DTG) for water-borne PU containing different amounts of GO.

Conclusions

The performance of a water-borne polyurethane containing different amounts of graphene oxide sheets has been investigated. Graphene oxide sheets are well dispersed in, and have good adhesion, with water-borne PU. This nano-filler markedly increases the modulus and yield strength of this polyurethane. Further, incorporation of graphene oxide sheets substantially reduces oxygen permeability and increases the thermal stability of this water-borne PU. In summary, graphene oxide sheets with their high-aspect ratio and exceptional properties is a good candidate for improving performance properties of water-borne polyurethane coatings.

Certain commercial products and instruments are described in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology.

References
1. S. Stankovich, et al., Nature, 442, 282 (2006).
2. S. Park and R. S. Ruoff, Nature Nanotech., 4, 217 (2009).
3. B.Z. Jang and A. Zhamu, J. Mat. Sci., 43, 5092 (2008).
4. 4. S. Park, et al., Chem. Mat., 20, 6592 (2008).
5. M. Celina and K.T. Gillen, Macromolecules, 38, 2754 (2005).